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Electroactive and Photoactive Nanostructured Materials From Self-Organizing Rod-Coil Copolymers: Synthesis and Electroluminescent Devices

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Electroluminescent ternary and binary rod-coil copolymer systems have been synthesized, characterized, and used to explore the effects of solid state supramolecular structure and morphology on the mechanism and quantum efficiency of electroluminescence. Enhanced electroluminescence due to efficient electronic energy transfer was observed in ternary rod-coil-rod copolymer systems containing two rodlike segments with different excitation energies, compared to the corresponding binary copolymers. Binary rod-coil copolymers which incorporate, into the rodlike segments, moieties that exhibit excited state intramolecular proton transfer were found to be electroluminescent via a novel mechanism, electrically generated intramolecular proton transfer (EGIPT). The inherent population inversion in the EGIPT process together with the observed stimulated emission imply the feasibility of electrically induced lasing in this class of materials. EGIPT was found to occur in only rod-coil copolymers with low rod-to-coil molar ratios, suggesting the profound effect of supramolecular structure.

The role of non-covalent interaction in dictating overall *supramolecular* structure in biopolymers is well established. Such interactions include, but are not limited to, hydrogen bonding, steric interactions, π - π interactions, dipole-dipole interactions, and van der Waal forces. A well known example is the double helical

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structure of DNA, which arises from hydrogen bonding. In proteins and other biopolymers, tertiary (supramolecular) structure, arising from non-covalent interaction, dictates function(1). Proteins and related biopolymers can only function properly if folded and packed into the correct geometry. Denaturing of these systems (disrupting the tertiary and secondary structures) disrupts the ability to perform their biological function(1). Nature has built sufficient flexibility into the macromolecular chains that allows folding to the requisite three-dimensional geometry.

Non-covalent interaction has profound effects on the structure and properties of synthetic molecules as well. The tendency of rod-like molecules to align coaxially through self-organization into liquid crystalline phases is just one example(2). This phenomenon has both positive and negative consequences. Liquid crystals display systems have successfully exploited the self-organizing features of anisotropic molecules(2b). In contrast, the tendency of conjugated rigid-rod polymers to aggregate in solution and as solids has complicated the investigation and development of these polymers for applications such as molecular composites (3-6) and electroluminescent devices (7-9). Because of the strong intermolecular interactions and aggregation of conjugated rigid-rod polymers, solubility in organic solvents is nonexistent, and the glass transition temperatures are extremely high, which makes processing difficult(4-6). Perhaps the most dramatic effect of aggregation in these conjugated rigid-rod polymers is the formation of ground state and excited state complexes, such as excimers and exciplexes, which profoundly influences all their photoelectronic properties(7-10). For example, the photoluminescence and electroluminescence spectra of thin films are strongly Stokes shifted compared to solution spectra and the fluorescence quantum yield is significantly reduced in the solid state(7-9).

To increase processibility, control aggregation and supramolecular packing in the solid state, and hence to regulate the electroactive and photoactive properties of conjugated polymer systems, we have adopted a strategy from Nature's example: *self-organizing rod-coil copolymers* that are analogous to proteins in terms of folding(10). Folding of the rod-coil copolymer chain and packing of its rigid segments in the solid state governs the photophysical properties(10). Variation of both the rod-to-coil ratio and lengths of the rod-like and coil-like segments, can be used to control the way in which conjugated segments assemble in the solid state. In this way, chromophore aggregation and excimer formation can be controlled and the wavelengths of emission and absorption can also be regulated. Moreover, the rod-coil copolymers have improved solubility in organic solvents relative to the parent conjugated rigid-rod homopolymers.

The efficacy of this "supramolecular engineering" strategy was first demonstrated for heterocyclic rod-coil copolymers, with poly(p-phenylenebenzobisthiazole) (PBZT) and derivatives used as the rod-like segments(10). The wavelength of absorption and emission of rod-coil copolymers

containing PBZT moieties could be tuned by the copolymer composition. Photoluminescence (PL) quantum yields could be increased by 600 % over the PBZT homopolymer, and fluorescence lifetimes increased, all of which can be attributed to the regulation of excimer formation through the supramolecular structure. Blending of such rod-coil copolymers with a conjugated homopolymer, into a nanocomposite, was shown to facilitate efficient singlet electronic energy transfer, a phenomenon which further increases the quantum efficiency of emission, and which can be used to regulate the emission wavelength(11).

Our prior studies(6-11) have now been extended to include investigation of the effects of supramolecular nanostructure on electroluminescence in rod-coil copolymers. The race to develop commercial light sources from organic polymers faces several challenges, among which are the issues of material stability, processibility, emission efficiency(14-16), device durability, and questions of the mechanism of electroluminescence(EL) (9, 12-15). The ease of processing of conjugated heterocyclic polymers, such as PBZT and its derivatives, using the Lewis acid complexation technique(16) or solubility in formic acid and related solvents, suggests them as a new class of electroluminescent polymers(9). Herein we report on the effects of supramolecular structure on electroluminescence of several rod-coil copolymers. The goals of this study included improvement of the EL properties of heterocyclic aromatic polymers by incorporating them into self-organizing rod-coil copolymers and exploration of the mechanism of electroluminescence in heterocyclic moieties known to undergo photoinduced intramolecular proton transfer.

Two new electroluminescent rod-coil copolymer systems are reported here. Ternary rod-coil-rod copolymers **1** and **2** (Chart 1), each of which contains two different electroactive and photoactive rigid-rod segments, are used to demonstrate the enhancement of electroluminescence through efficient electronic energy transfer. Comparative studies of binary rod-coil copolymers **3** and **4** (Chart 1), in which there is no energy transfer, confirmed the mechanism of PL and EL enhancement in the ternary copolymers. The second class of electroluminescent rod-coil copolymer system, **5**, is used to explore a novel EL producing chemical reaction, called electrically generated intramolecular proton transfer (EGIPT). The EGIPT process in these binary rod-coil copolymers, incorporating intramolecular hydrogen bonded chromophore **6** which is known to exhibit excited state intramolecular proton transfer, imply the feasibility of electrically induced lasing of such materials.

Experimental Methods

2,5-Diamino-1,4-benzenedithiol (DABDT) (Daychem or TCI) was purified by recrystallization from aqueous HCl as previously reported(17). Hydroxyterephthalic acid was prepared by the method reported by Miura *et al.*(18). Terephthalic acid (Fluka, > 99 %), 1,10-decanedicarboxylic acid (Aldrich,

99%), 1,4-phenylene diacrylic acid (Aldrich, 97 %), and 2,6-naphthalene dicarboxylic acid (Aldrich, 95 %) were used as received. Poly(phosphoric acid)(PPA) and 85 % phosphoric acid (ACS reagent grade, Aldrich) were used to prepare 77 % PPA, which was used as the polymerization medium. Phosphorus pentoxide (Fluka) was used as received. The copolymers were synthesized by condensation copolymerization in polyphosphoric acid of the tetrafunctional monomer, DABDT, with aromatic and aliphatic diacids, as previously described(10). The total molar quantity of the diacid was set to be equal to that of the DABDT, as required for high molecular weight copolymers. In the case of the nonhydroxylated binary(3, 4) and ternary(1, 2) copolymers, the coil-like fraction was set at 80 %, with the remaining 20% being composed of equal molar quantities of the remaining rod-like segments. The specific compositions of both 1 and 2 whose results are reported here are: $a=0.1$, $b=0.8$, and $c=0.1$ (see Chart 1). In the case of the intramolecularly hydrogen bonded copolymers 5, the molar quantity of the rod-like moiety was varied between 1 and 100 %. Polymerization yields were quantitative in all cases.

The names of the rod-coil copolymers (Chart 1) used in this study are: poly(1,4-phenylenebenzobisthiazole-co-decamethylenebenzobisthiazole-co-(1,4-phenylene-divinylene)benzobisthiazole) (PBZT-co-PBTC10-co-PBTPV, 1); poly(2,6-naphthylenebenzobisthiazole-co-decamethylenebenzobisthiazole-co-(1,4-phenylene-divinylene)benzobisthiazole) (PNBT-co-PBTC10-co-PBTPV, 2); poly (1,4-phenylenebenzobisthiazole-co-decamethylenebenzobisthiazole) (PBZT-co-PBTC10, 3); poly((1,4-phenylenedivinylene)benzobisthiazole-co-decamethylenebenzobisthiazole) (PBTPV-co-PBTC10, 4); and poly (2-hydroxy-1,4-phenylenebenzobisthiazole-co-decamethylene - benzobisthiazole) (HPBT-co-PBTC10, 5). The molecular structures and compositions of all the rod-coil copolymers 1-5 (Chart 1) were established primarily by ^1H NMR and FTIR spectroscopies, thermal analysis (TGA, DSC), intrinsic viscosity and various other spectroscopic measurements, as previously done for related polymers (10, 11,17). These characterizations confirmed the structures and compositions of Chart 1.

Optical absorption spectra of thin films were obtained with a Perkin-Elmer Model Lambda 9 UV/Vis/NIR Spectrophotometer. Steady state photoluminescence studies were performed by using a Spex Fluorolog-2 Spectrofluorometer equipped with Spex DM3000f Spectroscopy computer. The polymer films were positioned such that emission was detected at 22.5° from the incident radiation beam. Thin films of good optical quality were prepared by spin coating of polymer solutions in formic acid onto fused silica, followed by heating under vacuum to remove solvent. Picosecond transient absorption spectroscopy was performed as described elsewhere(19). Briefly, the transient absorption system consisted of a Continuum PY61 Series Nd:YAG laser utilizing Kodak QS 5 as the saturable absorber to produce laser light pulses of ~ 25 ps FWHM. These output pulses were then amplified and the third harmonic generated (355 nm).

Dichroic beamsplitters in conjunction with colored glass filters were used to isolate the fundamental (1064 nm) and the harmonic. The fundamental was directed along a variable optical delay and then focused into a 10 cm quartz cell filled with H₂O/D₂O (50:50) to generate a white light continuum probe pulse. The excitation and probe pulses (*ca.* 2 mm diameter) were passed approximately coaxially through the sample. The probe pulse was directed to a Spex 270 M monochromator through a Princeton Instruments fiber optic adapter and dispersed onto a Princeton Instruments dual diode array detector (DPDA 512). This allowed ~350 nm of the visible spectrum to be collected in a single experiment. A ST-121 detector controller/interface was incorporated into a 386/25 MHz PC to control the arrays and for data storage, manipulation and output. Correction for ambient lighting was made by subtracting the spectrum obtained when neither a pump pulse nor a probe pulse passed through the sample, whereas sample fluorescence was corrected for by subtracting the spectrum obtained by passing a pump pulse (with no probe pulse) through the sample.

The EL devices investigated consisted of bilayer polymer thin films sandwiched between two electrodes. To prepare the light-emitting diodes(LEDs), a layer of approximately 500 Å poly(vinyl carbazole) (PVK) was deposited on ITO (indium tin oxide) coated glass substrate (the anode) by spin coating from chloroform solution. The PVK layer functions as the hole transporting and electron blocking layer to confine electrons within the emissive layer. A 500-700 Å emissive layer of rod-coil copolymer was then spin coated from formic acid solution. Since the copolymers were insoluble in chloroform and PVK was insoluble in formic acid, no interfacial mixing occurred between the layers. An aluminum electrode (the cathode) of 500 - 1000 Å thick and *ca.* 7 mm² in area was thermally evaporated onto the device at high vacuum (4×10^{-6} torr). In the case of the intramolecularly hydrogen bonded copolymers 5, EL spectra were recorded with a Spex Fluorolog-2 Spectrofluorometer equipped with Spex DM3000f spectroscopy computer. Current-Voltage and luminance-voltage curves were recorded simultaneously by connecting an HP4155A semiconductor parameter analyzer together with a Grasby S370 optometer equipped with a luminance sensor head. In the case of binary and ternary copolymers 1-4, EL spectra were obtained by using a calibrated PR-650 colorimeter, whereas brightness was measured by using a Silicon Avalanche Photodiode (APD). The EL quantum efficiencies were calculated using the method proposed by Greenham *et al.*(20). No correction was made for losses due to absorption, reflection, or waveguiding effects of the glass. The values given therefore represent lower limits of the efficiency in terms of photons emitted per charge injected. All measurements were performed under ambient conditions.

Results and Discussion

Enhanced Electroluminescence By Energy Transfer. Rod-coil copolymer nanocomposites not only eliminate the formation of excimers, which quench luminescence, but they also allow for efficient singlet electronic energy transfer (EET), a process which leads to increases in the quantum yield of photoluminescence (PL) emission, and can be used in light-harvesting systems(11). Such polymer nanocomposites are therefore promising candidates for LED devices since EL and PL emission processes both originate from the same excited states species (7, 12). Ternary copolymers consisting of two different conjugated polymer segments and one flexible coil segment, such as 1 and 2 (Chart 1), should form nanostructured polymer assemblies at rod fractions below 0.4-0.5 as illustrated in Figure 1 (10). Efficient exciton transfer, from the rigid-rod component with the higher HOMO-LUMO energy gap, to the component with the lower HOMO-LUMO gap, should occur *via* Förster dipole-dipole interaction(11, 21). The component with the higher HOMO-LUMO energy gap thus acts as 'antennae' for harvesting and transferring the electronic energy to the component with the lower HOMO-LUMO gap, from which light is emitted. The singlet excitons involved are initially formed by either photoexcitation or by charge recombination induced by charge injection and transport(22).

The optical absorption and emission spectra of thin solid films of binary rod-coil copolymers 3e and 4e are shown in Figure 2. The overlap of the emission of 3e (donor chromophore) with the absorption of 4e (acceptor chromophore) suggests that a ternary copolymer system incorporating both the PBZT component of 3e (donor) and the PBTPV component of 4e (acceptor) will exhibit efficient Förster-type energy transfer(11). Figure 3 shows that this is in fact the case. The PL spectra of 3e and 4e, excited at 400 nm, and ternary copolymer 1, excited at 350, 370, 390, 440 and 460 nm, respectively, are shown. The lineshape and spectral position of the PL emission spectra of 1 are the same, regardless of the excitation wavelength(inset of Figure 3). The emission spectra of 1 resemble that of 4e, but are vastly different from 3e. The PL emission of 1 is thus dominated by the PBTPV component. Considering that the extinction coefficient of the PBZT component is higher than that of the PBTPV component between 370 and 390 nm (Figure 2), extensive energy transfer from the PBZT component must occur in this nanocomposite copolymer system. The relative PL quantum efficiency of 1 is 50 % higher than 3e, suggesting that EET in the ternary copolymer nanocomposite system accounts for the enhanced PL quantum efficiency.

Figure 4 shows the EL spectra of the copolymers 1-3, which closely resemble the PL spectra shown in Figure 3: green emission occurs from 1 and 2, whereas blue-green emission occurs from 3e. (An EL spectrum of 4 could not be obtained due to insufficient light emission). The similarity between the PL and EL spectra for 1 confirms that EET *via* Förster dipole-dipole interaction occurs under conditions leading to EL as well PL.

Figures 5 and 6 show brightness-voltage and current-voltage (I-V) curves, respectively, for the LED devices whose EL spectra are shown in Figure 4. Under conditions of forward bias, the EL devices have turn-on voltages of 11-13V for the rod-coil copolymers 1-3. The I-V character of **1** shows two distinct regions as shown in Figure 6. Above the onset of electroluminescence at a field of 1×10^6 V/cm, the current increases rapidly until saturation is reached at current densities above 170 mA/cm^2 . This may arise from a regime of space-charge-limited current due to the finite mobility of charge carriers in the nanocomposites(23). This is especially important in nanocomposites where 80 mol% of the solid consists of the non-electroactive and non-photoactive coil-like segments. However, the data strongly show deviation from the tunneling injection mechanism of charge carriers across the Schottky depletion layer at the anode, which was shown to hold for p-type conjugated polymers such as poly (2,5-dialkoxy-phenylenevinylene)(24). The brightness of EL is roughly proportional to current, clearly indicating that the EL emission is due to the recombination of charge carriers injected from electrodes into the bulk of the copolymer film. Electroluminescence efficiencies, in terms of photons emitted per charge injected were 0.083% for **1** and 0.04% for **2**. These values are substantially higher than the value of 0.015% obtained for an LED employing the binary copolymer 3e as the emissive layer. This result suggests that EET in nanostructured rod-coil copolymer polymer systems can significantly enhance EL quantum efficiency. In this regard, it is noteworthy that EL spectra could not be obtained from similarly constructed devices employing the corresponding homopolymers (PBZT, PBTPV, and PNBT) as the emissive layers, due to insufficient emission.

Device architectures other than the bilayer assembly (ITO/PVK/copolymer/Al) were also investigated, but did not give satisfactory results. Single copolymer devices (ITO/Copolymer/Al) had low emission levels, indicating a large imbalance in carrier injection or transport(25). When an additional layer of PVK was introduced as a hole transporting and electron blocking layer, device brightness was enhanced by at least one order of magnitude, suggesting that the carrier injection and transport were more balanced, and confirmed that the copolymers were electron-transporting materials.

EGIPT and Proton Transfer Electroluminescence. The second class of electroluminescent self-organizing rod-coil copolymers we have investigated, **5**, incorporates moieties such as **6** which exhibits excited state intramolecular proton transfer (ESIPT)(26-29). A simplified representation of the ESIPT process is shown in Scheme 1. Intramolecularly hydrogen bonded molecules such as 2-(2'-hydroxyphenyl) benzothiazole (HBT, **6**), which exist exclusively in the enol form (E) in the ground state, rapidly tautomerization from E* to the keto form (K*) upon photoexcitation to the first singlet excited state. The proton transfer occurs in less than a picosecond(30), resulting in a population inversion. The K* form can isomerize to a twisted state, and intersystem crossing to the triplet manifold is

also possible. Deactivation of the K^* states by an emissive pathway occurs with a Stokes shift of approximately 6000 cm^{-1} . Reverse proton transfer in the ground state to regenerate the starting E form completes the cycle. The fact that the process is a closed loop which regenerates the starting material after each cycle means that ESIPT is inherently a photostabilizing process. ESIPT has thus been exploited as a mechanism for protecting polymers from photochemical degradation(31-34) (e.g. yellowing when exposed to sunlight). The population inversion of the keto tautomer (Scheme 1) enables some intramolecularly hydrogen bonded molecules, such as 3-hydroxyflavone, to be employed as laser dyes(35,36), as was suggested initially by Khan and Kasha(37).

Conjugated polymers with intramolecularly hydrogen bonded moieties, such as **6**, incorporated into the main chain were prepared with the objective of developing robust materials for organic polymer light sources. Those studies showed that ESIPT in polymers is complicated by the effects of concentration quenching, extended conjugation, and competition with excimer formation(38). In order to investigate the effects of molecular structure and supramolecular nanostructure on PL and EL properties of ESIPT polymers, rod-coil copolymers **5** were synthesized with PBTC10 as the coil-like component and HPBT as the rod-like component. Preliminary findings showed that ESIPT occurred in the 5 % HPBT copolymer **5b**(39). The emission spectrum was due to the K^* form: emission from competing species was not significant. This copolymer(**5b**) was also shown to be electroluminescent via a new chemical reaction, electrically generated intramolecular proton transfer (EGIPT). Here we discuss how changes in the copolymer composition, from 1% to 100 % HPBT, affect the supramolecular structure and the attendant PL and EL of the solid state copolymers.

UV spectra of thin solid films of the copolymers **5** are shown in Figure 7. The variation of band shape and the energy of the absorption band with copolymer composition corresponds well with the effects seen in the case of the corresponding non-hydroxylated copolymers **3**(10). As expected, there is a steady increase in the HPBT absorption bands at 375, 395 and 421 nm, for compositions up to 40 %, with λ_{max} at 395 nm. For the 75 % copolymer and 100 % HPBT homopolymer, λ_{max} is at 445 and 450 nm, respectively, with a smaller peak occurring at 479 nm. In stark contrast to the shifting absorption λ_{max} , the PL spectra of these copolymers, shown in Figures 8 and 9, indicate a constant emission maximum. In the case of copolymers with low HPBT content (less than 40 %, Figure 8), the dominant 543-nm emission band, which is significantly Stokes shifted (*ca.* 6000 cm^{-1}) from the absorption, does not shift with composition. This peak clearly arises from emission of the excited keto tautomer (K^* in Scheme 1). Evidence for this assignment is as follows. First, the large Stokes shift between the emission band and the absorption band is typical of ESIPT processes leading to the keto state, a process very well known to occur for

intramolecularly hydrogen bonded molecules structurally similar to the HPBT component of **5**(29). In contrast, the corresponding copolymers without hydroxy side groups, which are not capable of ESIPT, have a much smaller Stokes shift, with the emission λ_{max} occurring at wavelengths shorter than 500 nm(10). Second, the transient absorption spectrum of **5b** (5% HPBT), shown in Figure 10, has a region of optical gain (stimulated emission) between 540 nm and 640 nm. The keto form K does not initially exist in the ground state, so formation of K* after excitation leads to a population inversion, facilitating observation of stimulated emission. This phenomenon has been well documented in molecules such as **6**(29).

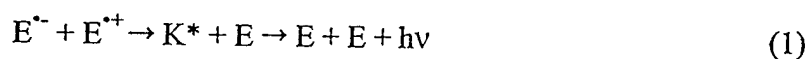
Upon increasing the HPBT content of the rod-coil copolymers, a number of trends in the PL properties can be seen. Optical gain, as determined by transient absorption spectroscopy, occurs only in the 1 % (**5a**) and 5 % (**5b**) copolymers. In copolymers with higher HPBT content, competition from transient absorption overwhelms the stimulated emission to the extent that no gain could be seen. Another phenomenon is that the minor bands at the blue end of the emission spectrum increase in magnitude and shift to longer wavelengths, relative to the 543 nm keto emission band (Figure 8). For copolymers with at least 40 % HPBT, the broad emission spectrum appears to be a single broad peak which is red shifted with increasing HPBT content (Figure 9). The origin of these bands is normal emission from E* (Scheme 1) in the case of copolymers with low HPBT content (<40%), which gives way to excimer emission from an (EE)* state in the high HPBT content copolymers. The excitation spectra of the blue end emission bands near 450-470nm match those of the keto emission band, suggesting that both bands arise from a common ground state.

We have previously demonstrated that extended conjugation inhibits ESIPT in polymers, forcing emission to occur from E*, due to an increase in the energy barrier on the excited state potential energy surface(38). It is possible that there is a potential energy barrier to proton transfer on the excited state potential energy surface of copolymers **5**, the magnitude of which increases with increases in conjugation length or HPBT content. This would lead to incomplete proton transfer and emission from both E* and K* (Scheme 1). As the HPBT content in the copolymer increases, the average conjugation length also increases, since the condensation polymerization technique leads to a statistical distribution of molecular weights. This increases the probability that ESIPT will not occur after photoexcitation, due to an unfavorably long conjugation length. The radiative deactivation thus occurs from E*, with a normal Stokes shift. The net result of this effect is an increase in the magnitude, and the shift to lower energies, of the blue end emission peaks. As the average conjugation length increases further, the magnitude of the ESIPT band relative to the E* bands decreases, until the point where ESIPT is completely prohibited. In these copolymers, with high HPBT content, the emission characteristics are similar to those of the corresponding non-hydroxylated copolymers(10). The red shift of the emission band, upon changing from 40 to 70 to 100 % HPBT, is clearly a result of the change of supramolecular

structure and morphology, and hence the increasing contribution of effects of aggregation and excimer emission(10).

The electroluminescent properties of copolymers 5 were also investigated(39). Figure 11 shows a representative EL spectrum obtained from a device employing 5b (5 % HPBT) as the emissive layer. The PL spectrum of the same copolymer is also shown. The PL and EL spectra match very closely, showing that EL emission originates from deactivation of K*. EL spectra for other copolymers 5 are shown in Figure 12. It is seen that the blue end bands, which were found in the PL spectra (Figures 8 and 9) are also found in the case of EL spectra, suggesting that wavelength and peak width of emission in the electroluminescence of the copolymers can be controlled through the composition and supramolecular nanostructure. The origin of the minor bands in the EL spectra cannot be from the PVK layer, which emits at 430 nm(40), because the minor bands are also seen in the PL spectra of films taken without a PVK layer. Instead, the origin of the blue-end bands is most likely the same as in the PL spectra. Current-voltage and brightness-voltage curves(not shown) track rather well for the copolymers 5, indicating that EL emission is due to the recombination of charge carriers injected from electrodes into the copolymer films.

The fact that emission occurs from a K* state, which is generated electrically rather than photochemically, is quite significant: these are the first materials reported to exhibit *electrically generated intramolecular proton transfer*, EGIPT. The mechanism of formation of K* by photoexcitation is well documented to occur by a rapid proton transfer from E*(29). However, the mechanism of formation of K* by the new EGIPT reaction is yet to be elucidated. The simplest representation of the overall EGIPT reaction is given in eq. 1.



Electrical injection of holes and electrons into 5 (at compositions which exhibit photoinduced ESIPT) results in the immediate generation of enol radical anions, E^{•-} and enol radical cations, E^{•+}. After this occurs, however, it is not clear whether K* forms simply through tautomerization of E*, or by combination of radical ions of the keto form which may arise from tautomerization of enol radical ions, of which many pathways can be supposed. The detailed mechanism of the observed EGIPT luminescence remains to be established.

Conclusions

The effects of supramolecular structure and morphology on electroluminescence of polymers have been investigated by means of novel ternary and binary rod-coil copolymers. Rod-coil-rod ternary copolymers with two differing rod components were shown to exhibit Förster-type excited state energy transfer, resulting in

about sixfold enhancement of the quantum efficiency of electroluminescence relative to the corresponding binary rod-coil copolymers. Further improvements of the electroluminescence quantum efficiency can be achieved by selecting the appropriate rigid-rod pairs in ternary copolymers, in which overlap between donor emission and acceptor absorption is maximized. Moreover, the space-charge-limited behavior of the EL devices of these rod-coil copolymers suggests that replacement of the inert nonactive coil by a hole transporting coil segment, the quantum efficiency and the brightness of the LEDs can be further improved. It was also demonstrated that both molecular and supramolecular structures influence the EGIPT reaction and proton transfer electroluminescence of rod-coil copolymers containing intramolecularly hydrogen bonded moieties. Although an electrically pumped diode laser based on EGIPT polymers is yet to be constructed, the preliminary EL results and the intrinsic population inversion in such materials suggest that it is a feasible concept.

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Literature Cited

- (1) (a) Richards, F. M. *Scientific Am.* **1991**, *January*, 54-63. (b) Kim, P. S.; Baldmin, R. L. *Ann. Rev. Biochem.* **1982**, *51*, 459-489.
- (2) (a) Flory, P. J. *Proc. Royal Soc. Lond. A* **1956**, *234*, 60. (b) Chandrasekhar, S. *Liquid Crystals*, 2nd ed; Cambridge University Press: New York, 1992.
- (3) Flory, P.J. *Macromolecules* **1978**, *11*, 1138-1141.
- (4) Wolfe, J.F. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 11, pp 601-635.
- (5) Arnold, F.E., Jr.; Arnold, F.E. *Adv. Polym. Sci.* **1994**, *117*, 257-295.
- (6) Roberts, M. F.; Jenekhe, S. A. *Chem. Mater.* **1994**, *6*, 135-145.
- (7) (a) Jenekhe, S.A.; Osaheni, J.A. *Science* **1994**, *265*, 765-768. (b) Osaheni, J.A.; Jenekhe, S.A. *Macromolecules* **1994**, *27*, 739-741.
- (8) (a) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 4726-4728. (b) Osaheni, J. A.; Jenekhe, S. A. *Chem. Mater.* **1995**, *7*, 672-682.
- (9) (a) Jenekhe, S. A.; Zhang, X.; Chen, X. L.; Choong, V.-E.; Gao, Y.; Hsieh, B. R. *Chem. Mater.* **1997**, *9*, In Press. (b) Zhang, X.; Kale, D. M.; Jenekhe, S. A. *Macromolecules*, Submitted.
- (10) (a) Jenekhe, S.A.; Osaheni, J.A. *Chem. Mater.* **1994**, *6*, 1906-1909. (b) Osaheni, J.A.; Jenekhe, S.A. *J. Am. Chem. Soc.* **1995**, *117*, 7389-7398.
- (11) Yang, C.J.; Jenekhe, S.A. *Supramolecular Science* **1994**, *1*, 91-101.

- (12) (a) Burroughes, J.H.; Bradley, D.D.C.; Brown, A.R.; Marks, R.N.; Mackay, K.; Friend, R.H.; Burn, P.L.; Holmes, A.B. *Nature* **1990**, *347*, 539-541. (b) Burn, P.L.; Holmes, A.B.; Kraft, A.; Bradley, D.D.C.; Brown, A.R.; Friend, R.H.; Gymer, R.W. *Nature* **1992**, *356*, 47-49.
- (13) Service, R.F. *Science* **1995**, *269*, 1042.
- (14) Zhang, C.; Braun, D.; Heeger, A.J. *J. Appl. Phys.* **1993**, *73*, 5177-80.
- (15) Zhang, C.; Von Seggern, H.; Pakbaz, K.; Kraabel, B.; Schmidt, H.W.; Heeger, A.J. *Synth. Met.* **1994**, *62*, 35-40.
- (16) (a) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216. (b) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419.
- (17) Osaheni, J.A.; Jenekhe, S.A. *Chem. Mater.* **1992**, *4*, 1282-1290.
- (18) Miura, Y.; Torres, E.; Panetta, C.A. *J. Org. Chem.* **1988**, *53*, 439-440.
- (19) Jenekhe, S.A.; Osaheni, J.A. *J. Phys. Chem.* **1994**, *98*, 12727-12736.
- (20) Greenham, N.C.; Friend, R.H.; Bradley, D.D.C. *Adv. Mater.* **1994**, *6*, 491-494.
- (21) Förster, T. *Ann. Phys.* **1948**, *2*, 55.
- (22) Pope, M.; Swenberg, C., *Electronic processes in Organic crystals*, Oxford University Press: New York, 1982.
- (23) Gruner, J.; Wittmann, H.F.; Hamer, P.J.; Friend, R.H.; Huber, J.; Scherf, U.; Mullen, K.; Moratti, S.C.; Holmes, A.B. *Synth. Met.* **1994**, *67*, 181-185.
- (24) Parker, I.D. *J. Appl. Phys.* **1994**, *75*, 1656-1666.
- (25) Parker, I.D.; Pei, Q.; Marrocco, M. *Appl. Phys. Lett.* **1994**, *65*, 1272-1274.
- (26) Weller, A. *Z. Elektrochem.* **1956**, *60*, 1144-1147.
- (27) Barbara, P.F.; Walsh P.K.; Brus, L.E. *J. Phys. Chem.* **1989**, *93*, 29-34.
- (28) See the special issues: *Chem. Phys.* **1989**, *136*, 153-360; *J. Phys. Chem.* **1991**, *95*, 10215-10524.
- (29) Formosinho, S.J.; Arnault, L.G. *J. Photochem. Photobiol. A: Chem.* **1993**, *75*, 21-48.
- (30) Frey, W.; Laermer, F.; Elsaesser, T. *J. Phys. Chem.* **1991**, *95*, 10391-10395.
- (31) Heller, H.J.; Blattmann, H.R. *Pure Appl. Chem.* **1973**, *36*, 141-161.
- (32) Werner, T. *J. Phys. Chem.* **1979**, *83*, 320-325.
- (33) Nir, Z.; Vogl, O. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 2735-2754.
- (34) O'Connor, D.B.; Scott, G.W.; Coulter, D.R.; Gupta, A.; Webb, S.P.; Yeh, S.W.; Clark, J.H. *Chem. Phys. Lett.* **1985**, *121*, 417-422.
- (35) Brucker, G.A.; Swinney, T.C.; Kelley, D.F. *J. Phys. Chem.* **1991**, *95*, 3190-3195.
- (36) Ferrer, M.L.; Acuna, A.U.; Amat-Guerri, F.; Costela, A.; Figuera, J.M.; Florido, F.; Sastre, R. *Appl. Opt.* **1994**, *33*, 2266-2272.
- (37) Khan, A.U.; Kasha, M. *Proc. Natl. Acad. Sci. USA.* **1983**, *80*, 1767-1770.
- (38) (a) Tarkka, R.M.; Jenekhe, S.A. *Mat. Res. Soc. Symp. Proc.* **1996**, *413*, 97-102. (b) Tarkka, R. M.; Jenekhe, S. A. *Chem. Phys. Lett.* **1996**, *260*, 533-538.

- (39) Tarkka, R.M.; Zhang, X.; Jenekhe, S.A. *J. Am. Chem. Soc.* **1996**, *118*, 9438-9439.
- (40) Hu, B.; Yang, Z.; Karasz, F.E. *J. Appl. Phys.* **1994**, *76*, 2419-2422.

Figure Captions

Figure 1. Schematic illustration of the protein-like folding (1) of an electroluminescent ternary rod-coil copolymer. The resulting self-organized nanostructure varies with copolymer composition (10).

Figure 2. Absorption and fluorescence spectra of thin films of 3e and 4e. ($\lambda_{\text{ex}} = 400 \text{ nm}$).

Figure 3. PL spectra of thin films of 1, 3e, and 4e ($\lambda_{\text{ex}} = 400 \text{ nm}$). Inset: PL spectra of thin films of 1 ($\lambda_{\text{ex}} = 350, 370, 390, 440, \text{ and } 460 \text{ nm}$, respectively) are identical at all excitation wavelength.

Figure 4. The electroluminescence(EL) spectra of thin films of copolymers 1, 2, and 3e.

Figure 5. Brightness-Voltage curves for 1, 2, and 3e.

Figure 6. Current-Voltage curves for 1, 2, and 3e.

Figure 7. UV spectra of rod-coil copolymers 5.

Figure 8. Photoluminescence spectra of copolymers 5a-5f. All copolymers were excited at 395 nm.

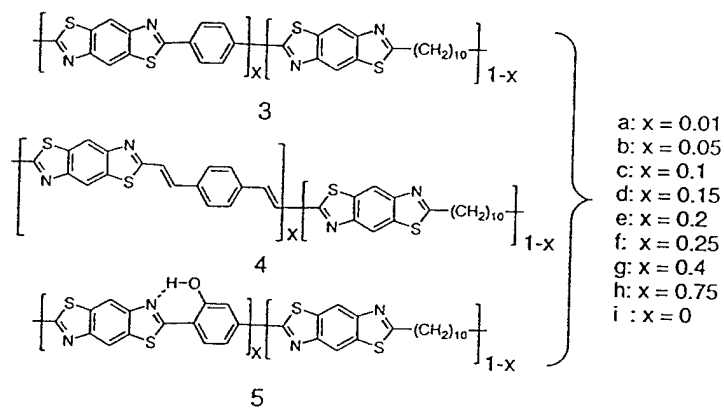
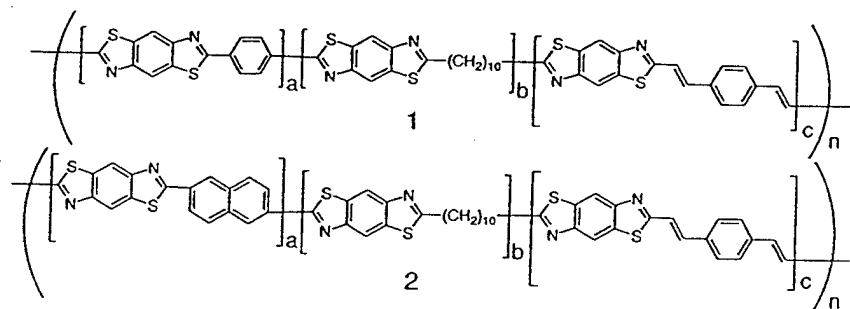
Figure 9. Photoluminescence spectra of copolymers 5g-5i. All copolymers were excited at 395 nm.

Figure 10. Transient absorption spectrum of 5b (5 % HPBT). ($\lambda_{\text{ex}} = 355 \text{ nm}$; delay = 50 ps).

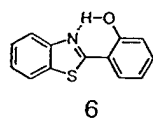
Figure 11. Electroluminescence(EL) and photoluminescence(PL) emission spectra of 5b (5 % HPBT).

Figure 12. Electroluminescence emission spectra of rod-coil copolymers 5 (1%, 5 %, 10 %, and 15 % HPBT; 5a, 5b, 5d, and 5e, respectively).

Chart 1



a: x = 0.01
b: x = 0.05
c: x = 0.1
d: x = 0.15
e: x = 0.2
f: x = 0.25
g: x = 0.4
h: x = 0.75
i: x = 0



Scheme 1

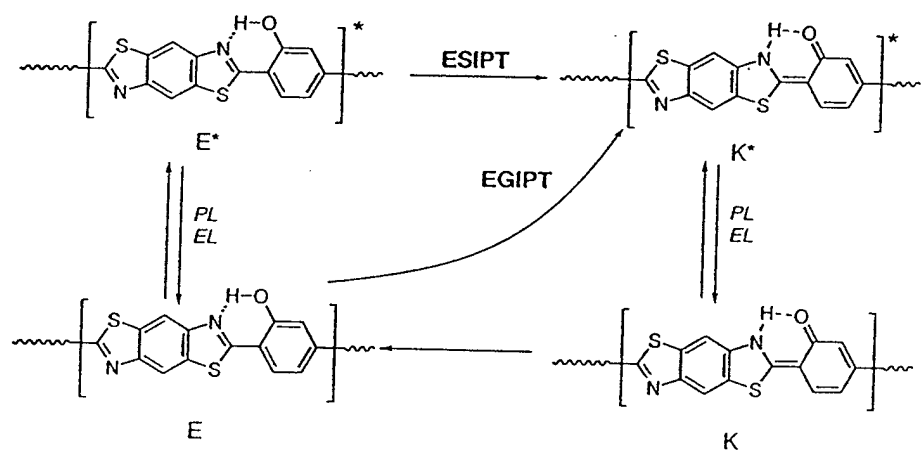


Fig. 1

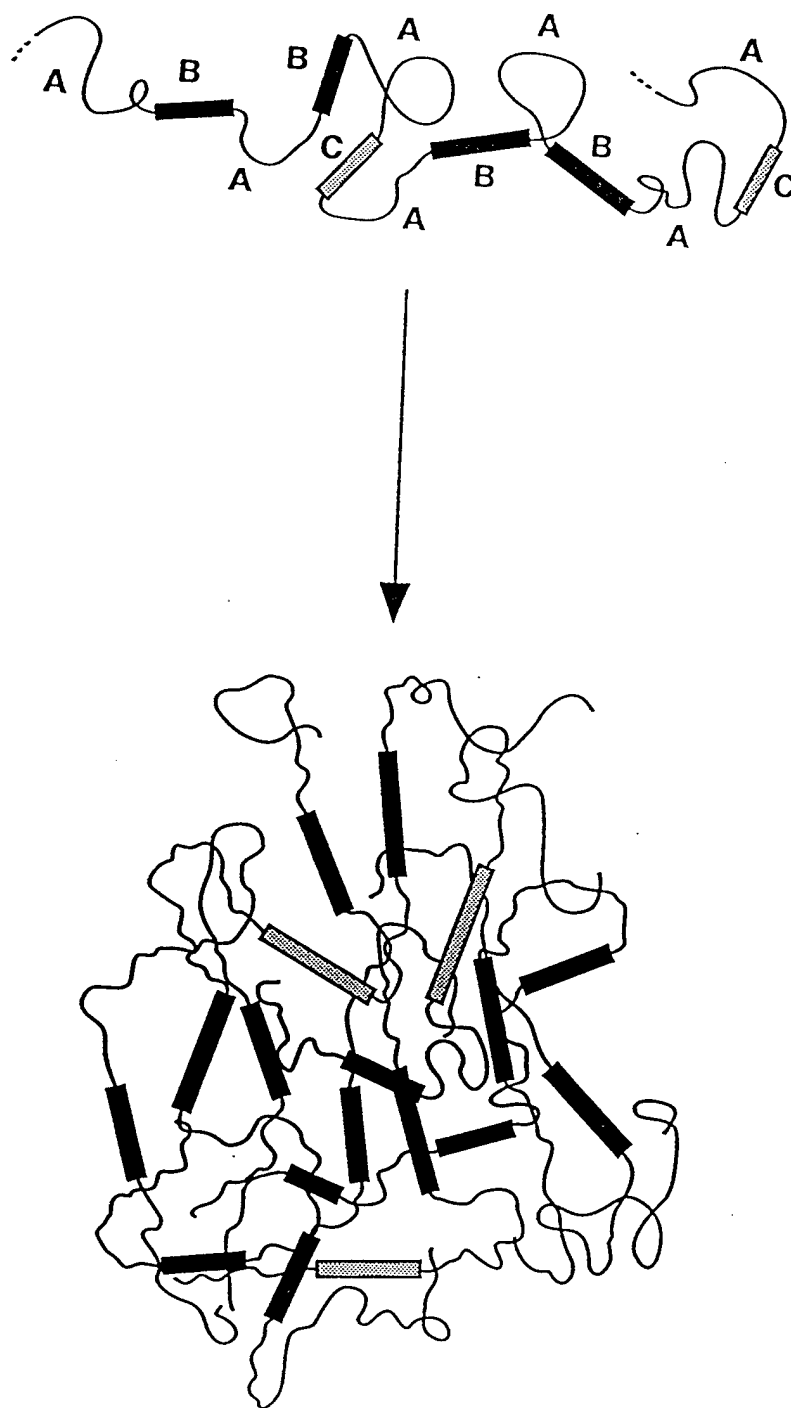


Fig. 2

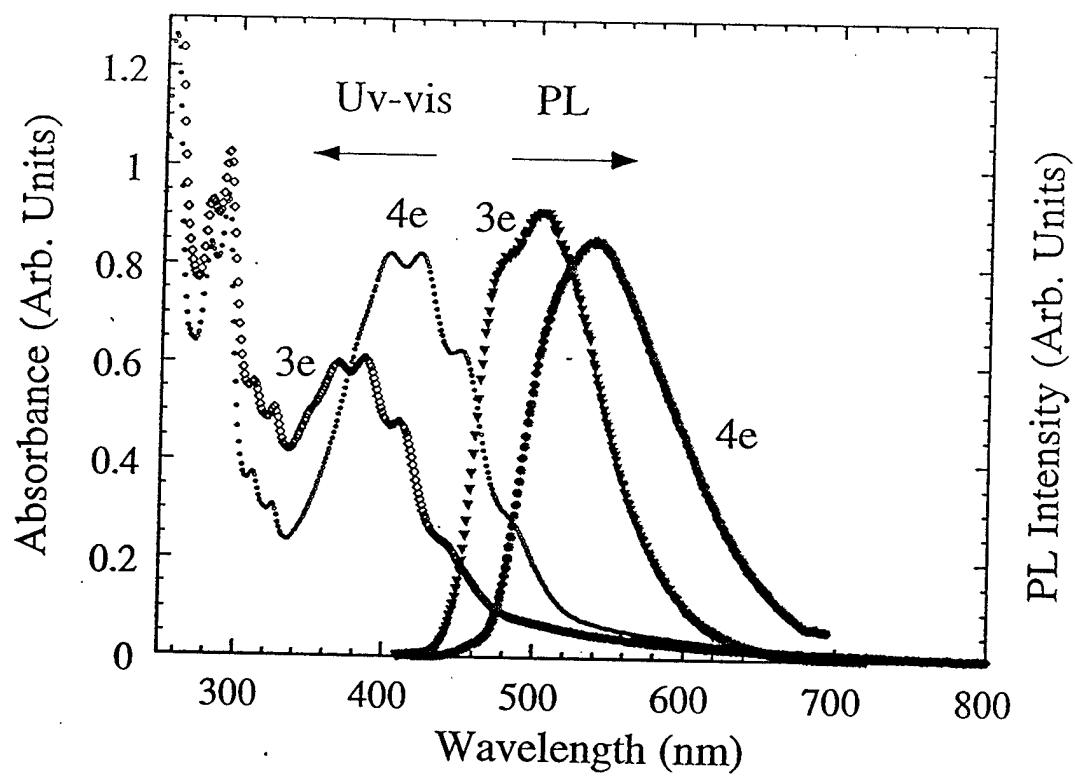


Fig. 3

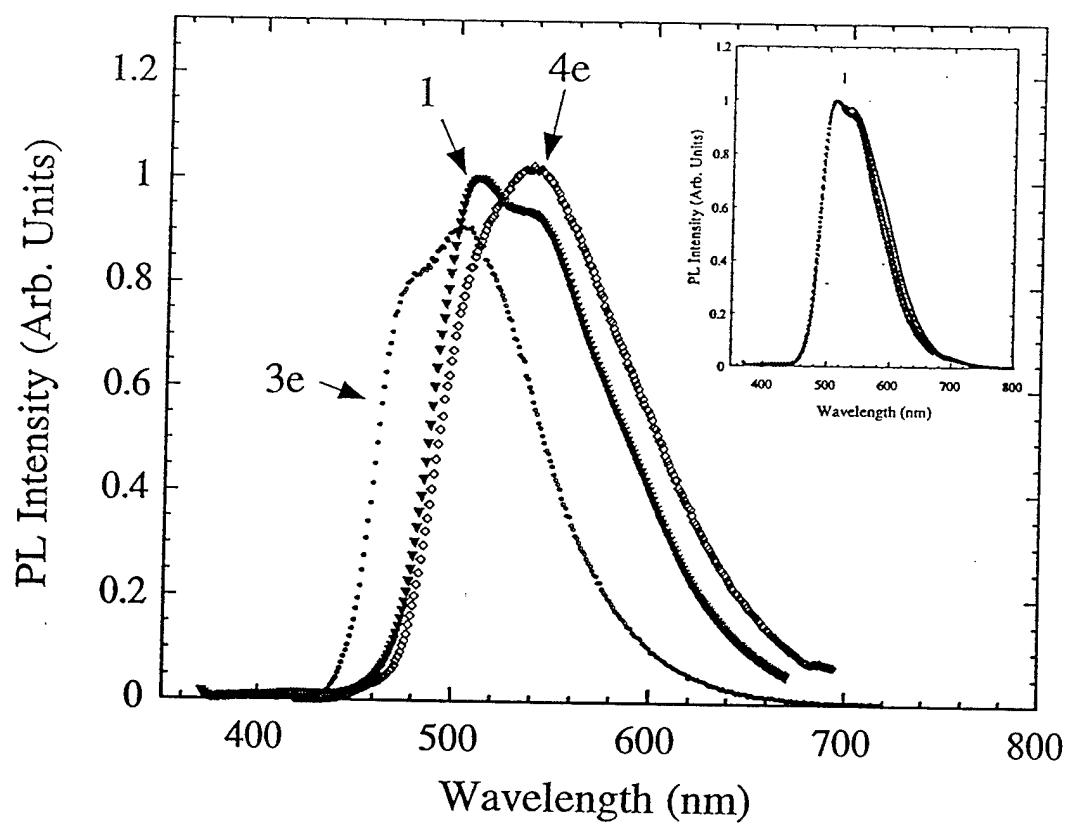


Fig. 4

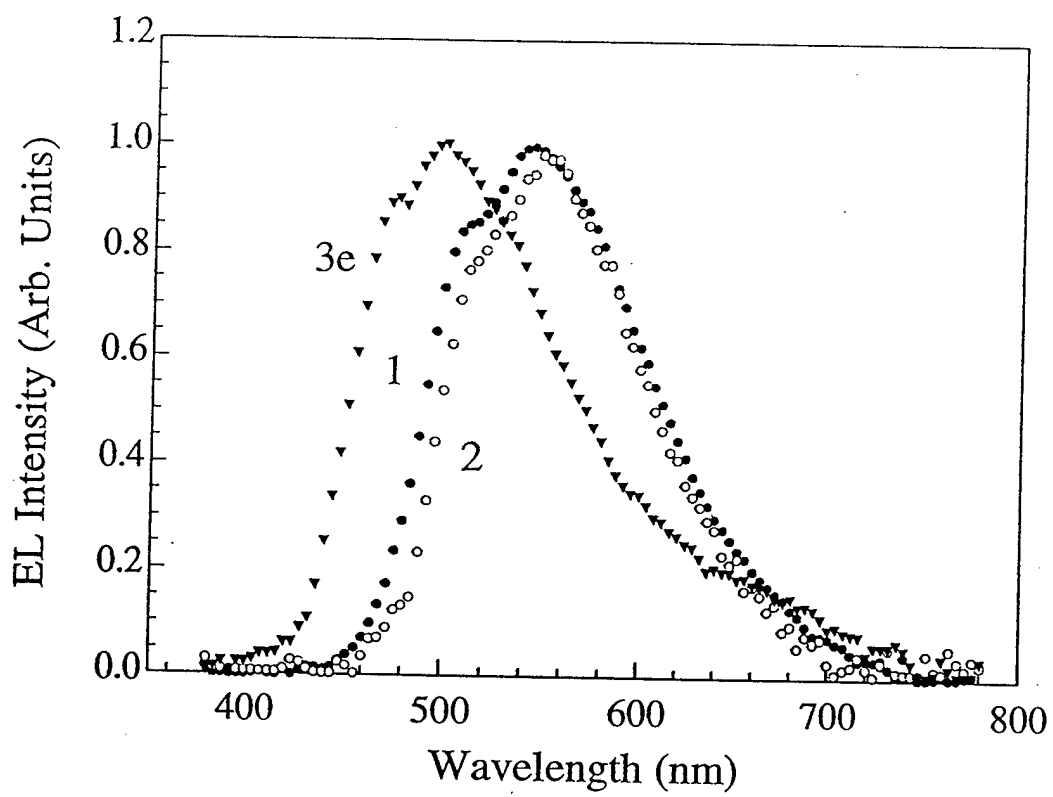


Fig. 5

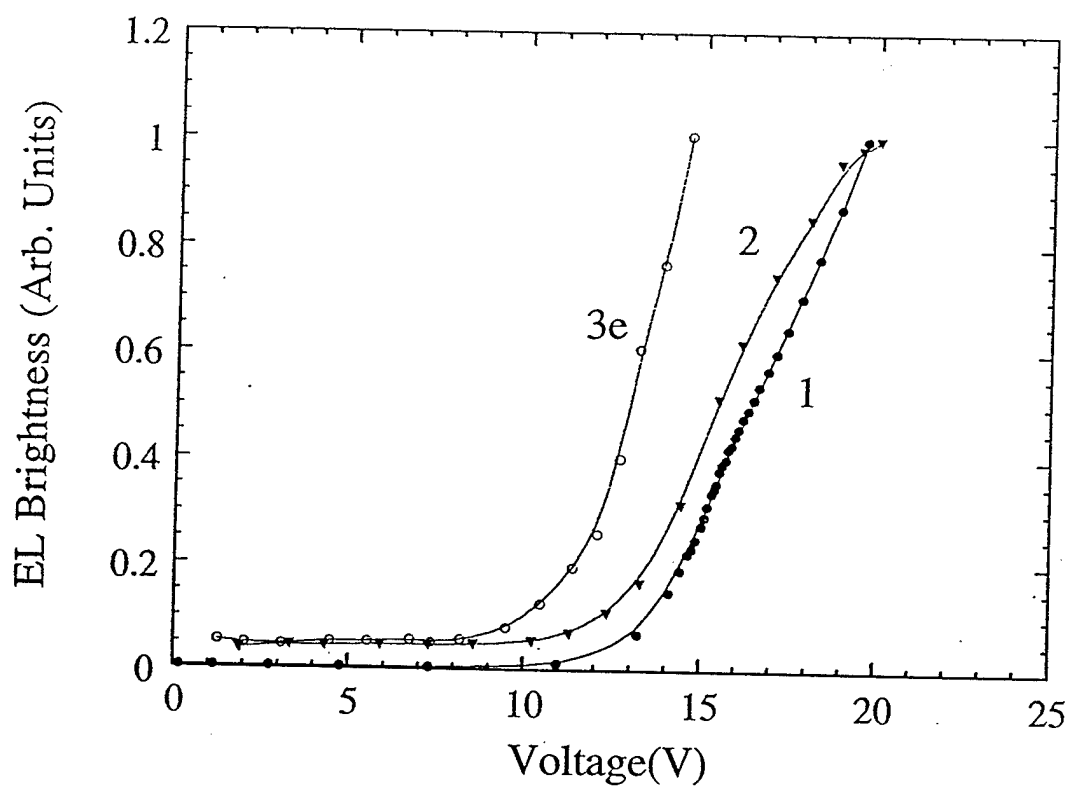
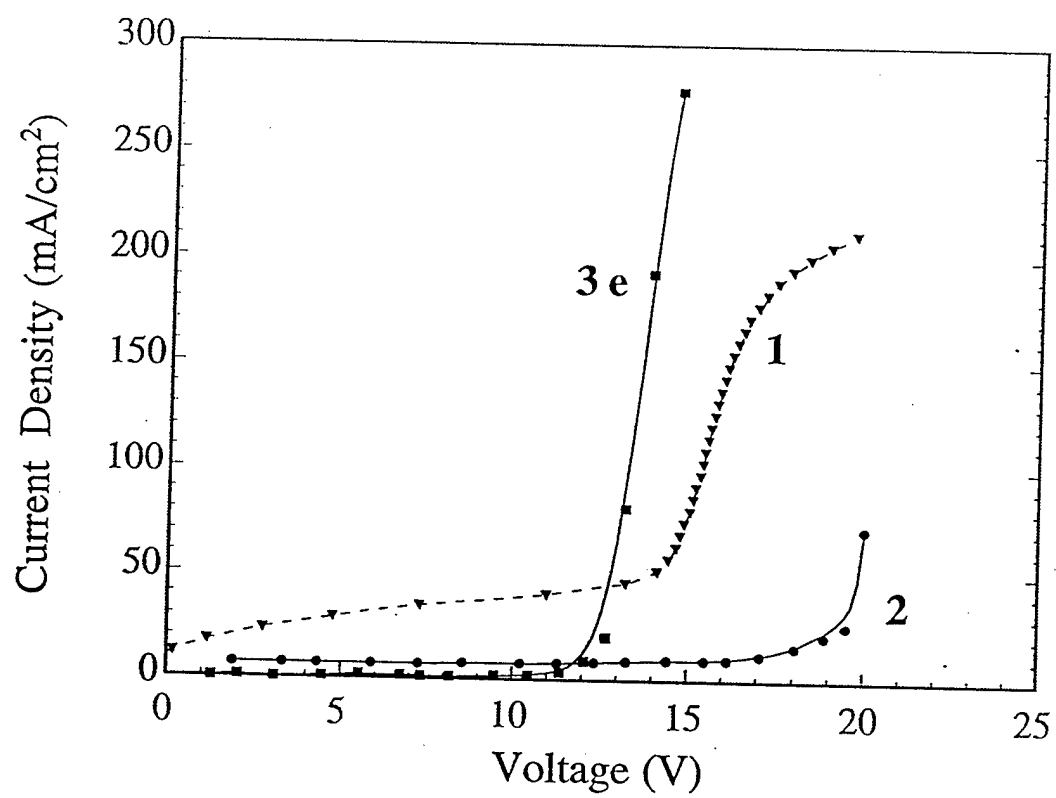


Fig. 6



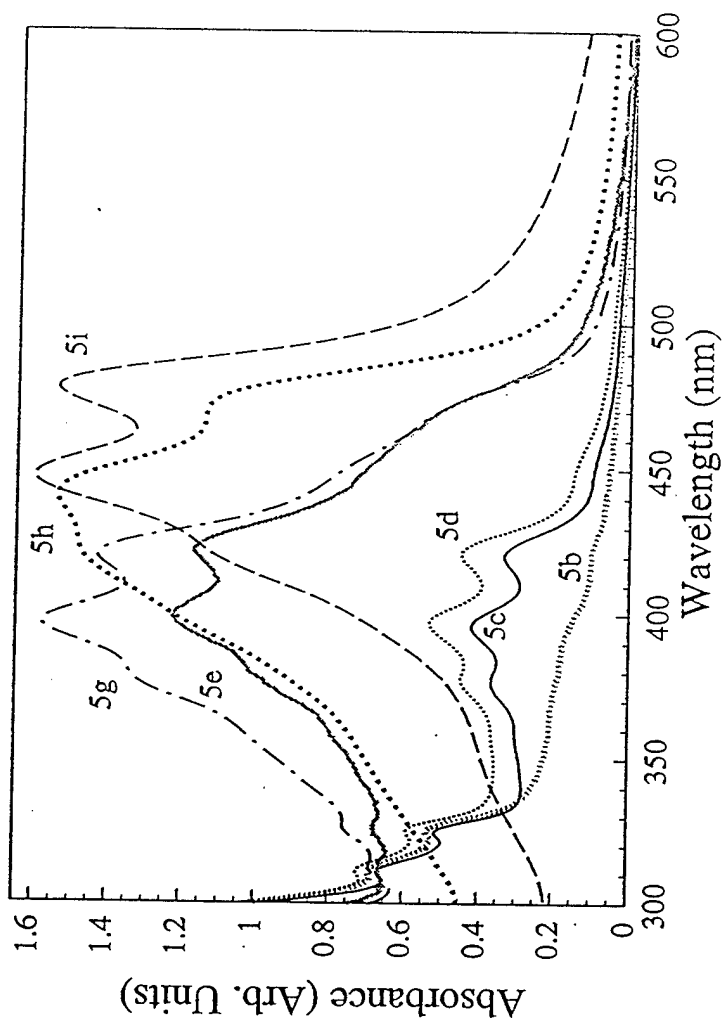


Fig. 8

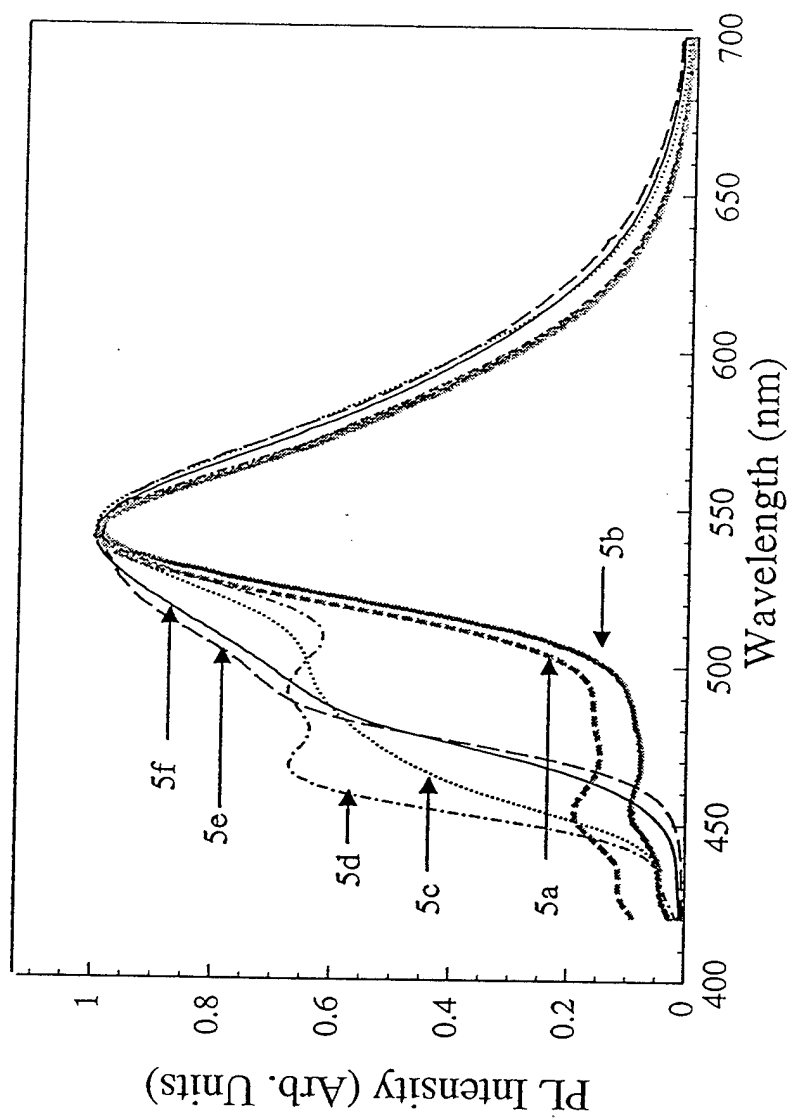


Fig. 9

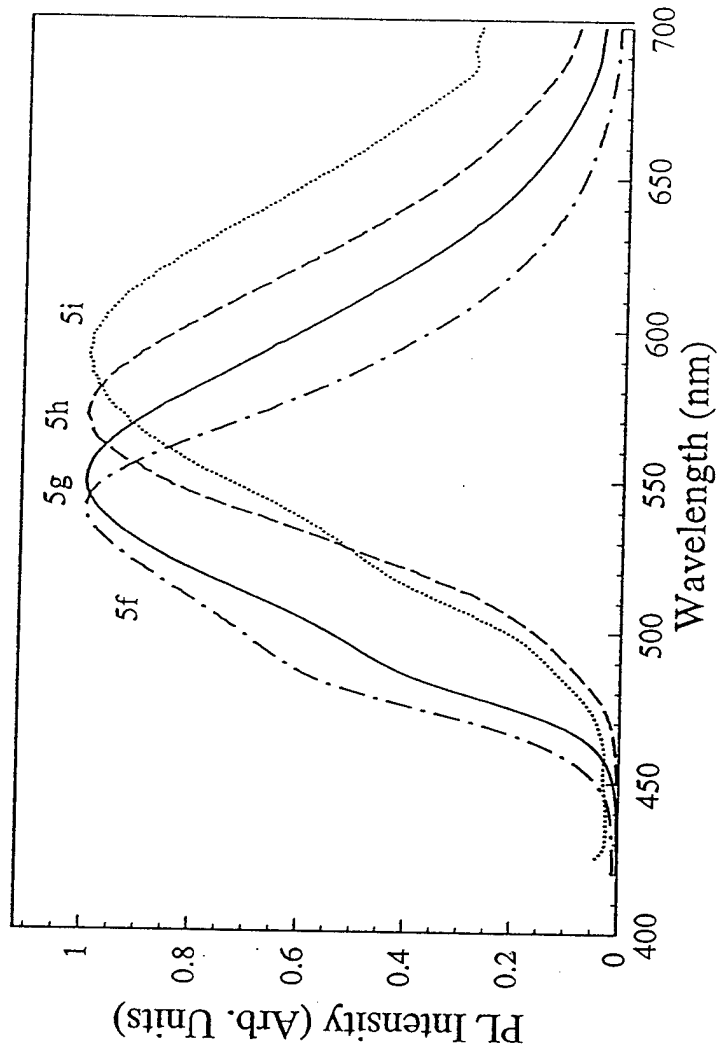


Fig. 10

